

# SCIENCE FOR CERAMIC PRODUCTION

UDC 666.792.32:623.093

## NEW SILICON CARBIDE BASED CERAMIC ARMOR MATERIALS

S. V. Zhitnyuk,<sup>1,2</sup> N. A. Makarov,<sup>1,3</sup> and T. V. Guseva<sup>1</sup>

Translated from *Steklo i Keramika*, No. 1, pp. 7 – 10, January, 2014.

---

An energy-efficient method of manufacturing strong composite materials based on SiC, modified with oxide eutectic additives, was developed. The effect of adding ultradisperse powder to commercial silicon carbide on the physical-chemical properties of ceramic was investigated. The ratio of silicon carbide and the sintering additive was determined. A dense, low-porosity, strong material was obtained. The ceramic obtained is a new construction material which holds promise for use as protective armor.

---

**Key words:** silicon carbide, eutectic additive, energy efficiency, sintering temperature, mechanical strength, crack resistance, body armor.

---

The developmental challenges of Russian industry presuppose the creation of technologies for fundamentally new materials supporting the development of different sectors of the economy. Traditionally, special high-strength steels and alloys were used in the development of body armor. They are characterized by high hardness and strength and relatively low cost, and with adequate thickness they are capable of effectively resisting all manner of damaging attack.

A drawback of such armor is its surface density (mass of the armor element per unit surface area). The mass of metallic armor is 2 – 3 times greater than that of modern ceramic armor with the same armor protection.

Hard and quite brittle materials such as ceramics are often more effective materials for body armor than steel or aluminum alloys. From the standpoint of protective properties and mass per unit area composite armor, i.e., external ceramic material, on a strong flexible substrate, surpasses steel and other metals. It is extremely important to increase the quality of ceramic armor for use in personal protection as well as protection in aviation and rocket engineering and transportation.

Protection for individuals or security personnel as well as for vehicles and equipment from bullets and so forth is a complicated technical problem. Aside from the requisite ballistic properties, protective armor must have a certain flexibility and low weight at an acceptable cost.

One of the most widely used oxygen-free materials in engineering is silicon carbide. Compared with other types of ceramic, silicon carbide possesses unique properties: high hardness, durability, thermal conductivity, fire resistance, strength, low linear thermal expansion coefficient, significant resistance to oxidation at temperatures to 1500°C, chemical inertness and corrosion and radiation resistance [1 – 3]; in addition, its density is 2.5 times lower than that of steel. Most importantly, it is relatively inexpensive.

However, unfortunately, temperatures 2150 – 2200°C are required to synthesize silicon carbide based ceramic. To develop energy efficient technologies for such ceramics eutectic additives that, after liquid-phase sintering, form a new high-heat-resistance solid phase as a result of chemical reactions between one another, the main phase and a gaseous medium were introduced into the materials. As a result the liquid phase vanishes and the high-temperature properties of the ceramic do not degrade during use.

A particularity of the method used to obtain new composite ceramic materials based on SiC is that special chemical methods are used to prepare nanopowders of oxide eutectic compositions which are subjected to prolonged mixing and mechanical activation together with oxygen-free compounds in order to obtain a uniform mixture of highly sintering-active powders.

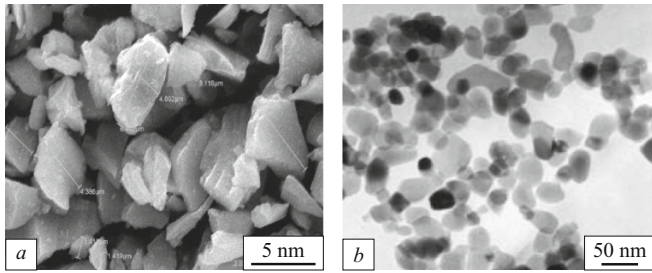
The combination of oxide eutectic additives and nanodisperse carbide powder makes it possible to create composite ceramic materials having improved physical and technical performance under intense, diverse, external actions. Ultradisperse crystallized phases of the eutectic make it possible

---

<sup>1</sup> D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia.

<sup>2</sup> E-mail: feanor42@ya.ru.

<sup>3</sup> E-mail: nikmak-ivmt@mail.ru.



**Fig. 1.** Microstructure of SiC powders: *a*) average grain size 3 – 4  $\mu\text{m}$ ; *b*) average particle size 45 – 55 nm.

to lower the sintering temperature, while the nanodisperse silicon carbide powder makes it possible to obtain the closest packing of particles during the formation of the samples, which imparts to the material very high strength, hardness and crack resistance. The eutectic compositions of the systems  $\text{CaO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  and  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  have appeared as such additives. Compositions with 80, 85 wt.% SiC and 15, 20 wt.%  $\text{CaO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  or  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  were used for the initial composition.

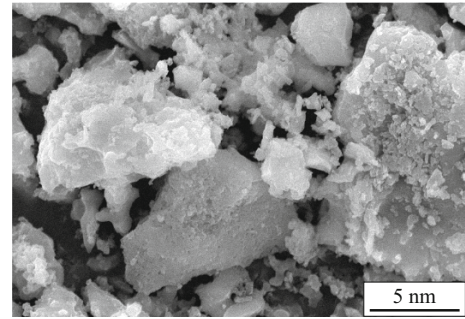
Silicon carbide with average grain size 3 – 4  $\mu\text{m}$  was used as the main raw material. Silicon carbide nanopowder with average grain size 45 – 55 nm was used as the ultra-disperse powder. The microstructure of the powder is presented in Fig. 1.

The initial materials used to synthesize the additives in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  were  $\text{CaCO}_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ . The amount of the initial materials was calculated in accordance with the calcination losses and the oxide chemical composition of the eutectic. The mixture with the working composition was loaded into teflon drums of a vibratory mill, mixed with acetone and comminuted with corundum balls. The obtained suspension was dried at room temperature, after which the material was passed through a capron sieve.

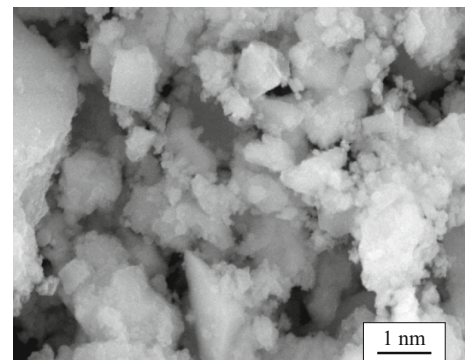
Differential scanning calorimetry showed that all processes involving intense physical-chemical transformations are completed by temperature 1300°C. For this reason the mixture of the initial components was calcinated at 1300°C. The powders obtained were dried and passed through a No. 05 capron sieve. X-ray phase analysis shows  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$  to be present in the additive.

In the case of synthesis, the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  additives aluminum-magnesium spinel and yttrium-aluminum garnet were obtained separately.

Petrographic studies of batches were performed at three calcination temperatures to determine the synthesis temperature of aluminum-magnesium spinel: 1100, 1200 and 1300°C. The results showed that the preferred temperature is 1100°C. Photographs of the microstructure of the synthesized spinel powder are presented in Fig. 2. Aluminum-magnesium spinel is represented by loose aggregates up to 10  $\mu\text{m}$  in size and average individual particle size about 500 nm.



**Fig. 2.** Microstructure of  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  spinel powders; synthesis temperature 1000°C.



**Fig. 3.** Microstructure of the co-precipitated hydroxides  $\text{Al}(\text{OH})_3$  and  $\text{Y}(\text{OH})_3$ .

To prepare yttrium-aluminum garnet by heterophase precipitation hydrated yttrium and aluminum chlorides were used as the initial materials. The salts taken in a ratio making it possible to obtain the compound  $\text{Y}_3\text{Al}_5\text{O}_{12}$  were dissolved in distilled water with heating to  $100 \pm 5^\circ\text{C}$ . The solution obtained was heated to mass fraction 90% of the maximum solubility at this temperature (the concentration of the solution was monitored with an areometer). Compressed nitrogen under pressure  $(1 - 2) \times 10^4 \text{ Pa}$  was used to spray the salt solution obtained at  $100 \pm 5^\circ\text{C}$  through a 1.0 – 1.5 mm in diameter glass capillary into a saturated solution of ammonia at  $-20^\circ\text{C}$ . The suspension obtained was transferred into a Büchner funnel and washed with distilled water to  $\text{pH} = 6.0$  in the filtrate. The residue was washed with acetone.

Photographs of the microstructure of the co-precipitated yttrium and aluminum hydroxides as well as the synthesized yttrium-aluminum garnet are presented in Figs. 3 and 4.

The powder of co-precipitated aluminum and yttrium hydroxides is represented by loose aggregates ranging in size from < 1 to 5  $\mu\text{m}$ . The synthesized powder consists of aggregates of size in the range 2 – 20  $\mu\text{m}$ , the average size being 7 – 10  $\mu\text{m}$ . The particle size is about 400 nm.

The ready additives from the systems  $\text{CaO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  and  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  were introduced into SiC powder. The mixtures obtained with the working composition were

**TABLE 1.** Properties of Samples of the Experimental Compositions

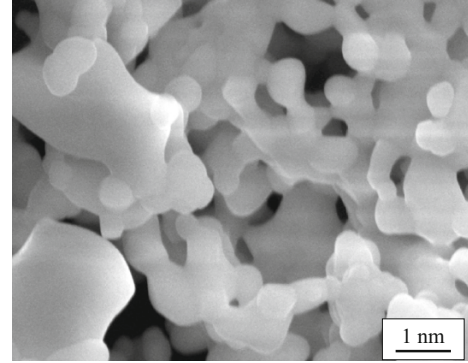
Additive		$\rho$ , g/cm <sup>3</sup>	$P_o$ , %	$\sigma_b$ , MPa
System	Mass fraction, %			
CaO–Al <sub>2</sub> O <sub>3</sub> –Y <sub>2</sub> O <sub>3</sub>	15	2.56	38.0	70 ± 18
	20	2.58	34.0	82 ± 20
MgO–Al <sub>2</sub> O <sub>3</sub> –Y <sub>2</sub> O <sub>3</sub>	15	2.60	34.0	100 ± 20
	20	2.70	28.0	120 ± 25

**TABLE 2.** Properties of Samples of the Experimental Compositions based on SiC with the Introduction of 30% nano-SiC

Additive		$\rho$ , g/cm <sup>3</sup>	$P_o$ , %	$\sigma_b$ , MPa
System	Mass fraction, %			
CaO–Al <sub>2</sub> O <sub>3</sub> –Y <sub>2</sub> O <sub>3</sub>	15	3.00	9.5	220 ± 25
	20	3.02	8.0	200 ± 18
MgO–Al <sub>2</sub> O <sub>3</sub> –Y <sub>2</sub> O <sub>3</sub>	15	3.04	7.5	350 ± 16
	20	3.05	5.0	310 ± 20

loaded into teflon drums of a vibratory mill, mixed with acetone and comminuted with corundum balls. The suspensions obtained were dried at room temperature, after which the material was passed through a No. 05 capron sieve. A solution of paraffin in carbon tetrachloride was used as a binder for pressing samples (the paraffin mass fraction was 5%). A mineral component was introduced into a hot solution of binder in proper proportions and then evaporated to complete removal of the solvent. The samples were molded at pressure 100 MPa. Calcination was done in argon at 1900°C. Prior to calcination heat-treatment was performed in a furnace with silicon carbide heaters at 700°C. The results of investigations of the properties of the samples are presented in Table 1: the average density  $\rho$ , the open porosity  $P_o$  and the maximum strength in bending  $\sigma_b$ .

Increasing the mass content of the additives CaO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> and MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> from 15 to 20% increases the density of the samples from 2.56 to 2.58 g/cm<sup>3</sup> and from 2.60 to 2.70 g/cm<sup>3</sup>, respectively. The introduction

**Fig. 4.** Microstructure of 3Y<sub>2</sub>O<sub>3</sub> · 5Al<sub>2</sub>O<sub>3</sub>.

of additives in the system MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> with other conditions remaining unchanged makes it possible to synthesize denser and less porous material.

For the same amount of modifier the mechanical strength of the ceramic obtained using magnesium-containing additive is 15 MPa higher on average, and the open porosity  $P_o$  5% lower on average than with a calcium-containing additive.

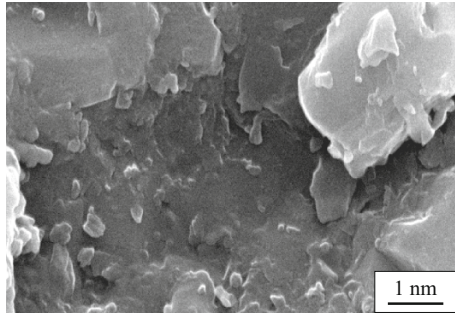
Nonetheless, the synthesized ceramic possesses significant porosity and low mechanical strength. The results of the investigations show that in all probability the activity of the initial silicon carbide is too low for synthesis of material with high mechanical properties. For this reason a decision was made to modify the structure of the ceramic by introducing high-activity ultradisperse silicon carbide powder synthesized by the plasma-chemical method (nano-SiC). The nano-SiC was introduced into the system in amounts 30 and 50% (mass fraction) with respect to the silicon carbide present so that the total SiC content in the batch remained unchanged. The properties obtained for the calcined samples are presented in Tables 2 and 3.

Ceramics with an ultradisperse component make it possible to significantly improve the ceramic properties and increase strength compared with ceramics without such a component. For example, irrespective of the amount of the eutectic modifier introduced, the mechanical strength for a material with 30 wt.% nano-SiC turns out to be higher and open porosity lower than in materials without an ultradisperse oxygen-free component. Apparently, this is associated with the fact that the introduction of ultradisperse com-

**TABLE 3.** Properties of Samples of the Experimental Compositions based on SiC with the Introduction of 50% nano-SiC

Additive		$\rho$ , g/cm <sup>3</sup>	$P_o$ , %	$\sigma_b$ , MPa	$K_{IC}$ , MPa · m <sup>1/2</sup>	$E_{el}$ , GPa	$HV$ , GPa
System	Mass fraction, %						
CaO–Al <sub>2</sub> O <sub>3</sub> –Y <sub>2</sub> O <sub>3</sub>	15	3.10	1.2	380 ± 20	3.8	345	21.4
	20	3.12	1.3	355 ± 15	3.7	340	21.6
MgO–Al <sub>2</sub> O <sub>3</sub> –Y <sub>2</sub> O <sub>3</sub>	15	3.12	0.4	450 ± 25	4.0	380	22.4
	20	3.55	0.3	400 ± 28	4.2	360	21.8





**Fig. 5.** Microstructure of SiC-based ceramic with 15 wt.% MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> and 50 wt.% ultradisperse nano-SiC.

ponents changes the structure formation process during compaction and activates the sintering process, which makes it possible to increase the strength of ceramic.

The values of the density and porosity in materials containing different eutectic additives have similarities but a break is observed in the porosity values, which other conditions being equal increases with increasing content of the ultradisperse component nano-SiC. The investigation showed that increasing the mass content of CaO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> and MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> from 15 to 20% increases the density and porosity by small amounts but lowers the ultimate strength in bending appreciably.

The parameters obtained for samples with 50% mass content of nano-SiC and with an MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> additive tend toward the values specified for armor materials — open porosity close to zero and ultimate strength in three-point bending  $450 \pm 25$  MPa.

Properties very important for armored protection were determined for compositions containing 50% nano-SiC: the fracture toughness  $K_{IC}$ , the modulus of elasticity  $E_{el}$  and the Vickers hardness  $HV$  (see Table 3).

In summary, the optimal experimental composition is a ceramic with 15 wt.% eutectic additive in the system MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> and 50 wt.% ultradisperse SiC.

It is this ceramic that was picked as preferred for armor material. The microstructure of the ceramic with the composition indicated is presented in Fig. 5.

Electron microscopy shows that the average size of the silicon carbide crystals of the material developed is  $5 - 6 \mu\text{m}$ , and the size of the crystals of aluminum-magnesium spinel, yttrium-aluminum garnet and corundum, which are constituents of the eutectic additive, is less than  $1 \mu\text{m}$ , the closed porosity is intercrystalline and rounded, the average pore size is  $\ll 1 \mu\text{m}$  and the amount of pores is  $1 - 2\%$ .

In summary, it can be concluded that the ceramic technology developed on the basis of silicon carbide with 15 wt.% eutectic additive from the system MgO–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> and 50 wt.% nano-SiC, which possesses fine-crystalline structure, ultimate strength in three-point bending  $450 \pm 25$  MPa, microhardness 22.4 GPa and sintering temperature  $1900^\circ\text{C}$ . This ceramic has promise for use as a construction material as well as an armor material.

*The work was supported by the Ministry of Education and Science of the Russian Federation under contract GK 16.552.11.7046.*

*We are deeply grateful to O. B. Petrova, Candidate of Technical Sciences and Associate Professor in the Department of Chemistry and Technology of Crystals at the D. I. Mendeleev Russian Chemical Technology University, for assistance in determining the microhardness.*

## REFERENCES

1. Yu. D. Tret'yakov, "Ceramics: past, present and future," *Khimiya: Soros. Obrazovat. Zh.*, No. 6, 53 (1998).
2. F. Matthews and R. Rolings, *Composite Materials: Mechanics and Technology* [Russian translation], Tekhnosfera, Moscow (2004).
3. V. L. Balkevich, *Technical Ceramics* [in Russian], Stroiizdat, Moscow (1984).